

SUBSTITUTE SPECIFICATION**METHOD AND DEVICE FOR LIBERATING OXYGEN ISOTOPES
FROM OXYGEN-CONTAINING SOLIDS****SPECIFICATION****CROSS REFERENCE TO RELATED APPLICATIONS**

5 This application is a national phase of PCT/DE 00/00
425 filed 11 February 2000 and is based upon a German national
application 199 06 732.5 filed 18 February 1999 under the
International Convention.

FIELD OF THE INVENTION

10 The invention relates to a method of liberating oxygen
isotopes from oxygen-containing solids, especially from biogenic
and nonbiogenic silicate-based substances or solids as well as TO
an apparatus suitable for carrying out the method.

BACKGROUND OF THE INVENTION

15 In paleoclimatology and paleothermometry there is
interest in determining the proportions of the oxygen isotopes
 ^{16}O and ^{18}O in solid samples.

From the work "Stable Isotope Geochemistry" of J.
20 Hoefs, 4th Completely Revised, Updated and Enlarged edition,
Springer, Berlin, Heidelberg, New York, Barcelona, Budapest, Hong
Kong 1997, various methods of liberating oxygen from samples are
known. Thus silicate-based samples of solids to be investigated
are evaporated according to the state of the art, whereby oxygen
25 is liberated and the analysis can proceed therewith. The oxygen
can be investigated directly by mass spectroscopy as to its

isotopes. Alternatively, the oxygen can be transformed in a further reaction with carbon into CO or CO₂. The determination of the isotope ratio is then effected by mass spectroscopic investigation of the CO or CO₂ resulting from reaction with graphite.

Another method which has come into use mainly with silicates and oxides is based upon the fluorination of the substances whose oxygen isotopes are to be analyzed. In this case, the oxygen is liberated by means of F₂ or BrF₃ in nickel cylinders at 500 to 600°C. The oxygen thereafter is generally transformed to CO₂ on hot graphite and is then subjected to the mass spectroscopic measurement. Frequently the sample to be investigated requires a prepurification, because foreign molecules or groups which are detrimental to the analysis can be incorporated in the sample. Thus, for example biogenic silicates like the shells of diatoms frequently contain water or OH groups which make an analytic oxygen isotope determination very difficult. Should an analysis of the isotope composition of the oxygen nevertheless have to be carried out, the samples frequently initially must be freed from the foreign substances or molecules by preliminary purification steps which can falsify the analysis result. A method of liberating oxygen from the sample to be tested is the laser vaporization of partial regions of solids. In this method it is not possible to avoid a slight fractionation, which means a shift in the oxygen isotope ratio of the solid sample to be analyzed and which is based upon the somewhat different conditions in the boundary regions of the evaporation process. The heating of the solid sample by laser has therefore significant drawbacks with respect to the representativity or reproducibility of the results with large

samples which can be heated only at point-like regions of the entire solid sample by the laser beam and thus makes the isotope analysis accessible. In the case of inhomogeneities in a sample, the results of the respective measurements of the ratios of the oxygen isotopes are not truly representative for the entire sample. To obtain representative results, therefore, many measurements are required whose results must be averaged.

OBJECT OF THE INVENTION

It is therefore the object of the invention to provide a method and an apparatus by means of which solid samples, above all biogenic silicates or biogenic silicon dioxide, can be analyzed in a single operation without pretreatment especially to liberate from the sample adhering H₂O molecules or OH groups, and also without the need for averaging the results.

SUMMARY OF THE INVENTION

This object is attained in a method of liberating oxygen isotopes from oxygen-containing solids in which the solids are heated by being brought into contact with graphite and subjected to induction heating whereby CO and/or CO₂ result.

With the method according to the invention it is possible directly to obtain results for the ratio of the isotope oxygen composition in solid samples of such problematical materials like biogenic silicates in a sequence collectively forming a single operation. It is therefore no longer necessary to have any special separate experimental steps of the preparation of the sample. Consequently, a significant

reduction in the work and time requirements is possible. In addition, the method of the invention enables the analysis of the oxygen isotope ratios of samples without having to deal with the inhomogeneities of the sample on the quality of the measurement results with respect to the complete sample. Apart from quantities which are measurable by mass spectroscopy in a problem-free manner, the sample quantities for example for silicate in flow mode can be reduced to 50 μg SiO_2 , which cannot be as easily handled with chemical decomposition methods. With very heterogeneous samples, however, larger samples of at least 100 μg SiO_2 , or more are preferred to permit a reliable mean value to be obtained.

According to the invention, the heating up of the solids is effected in vacuum. The CO or CO_2 resulting from the heating of the solids can be isolated. The CO or CO_2 can be fed to an analysis process which preferably is a mass spectroscopic process. The solid can be a silicate and the heating can be carried out from 1600 to 2200°C. Preferably, the heating is carried out sequentially to drive off impurities like water. An apparatus for liberating oxygen isotopes from oxygen-containing solids can include a graphite crucible and an induction source. The graphite crucible can be provided in a vacuum-tight housing of quartz glass to which a pump is connected. The apparatus can comprise means for capturing gaseous CO or CO_2 arising from induction. The housing of quartz glass can be provided with means for cooling it. The housing can be opened on opposite sides to replace the solid with the graphite crucible. The graphite crucible can be elongated whereby at an upper end a cavity is provided for receiving the solids and at the opposite

end an axial bore is provided which can receive a rod with which the graphite crucible can be mounted in, the housing.

BRIEF DESCRIPTION OF THE DRAWING

The sole FIGURE of the drawing is a cross sectional
5 view of an apparatus according to the invention.

SPECIFIC DESCRIPTION

The apparatus according to the invention shown in FIG. 1 comprises a graphite crucible 1 which is elongated, whereby at the upper end a cavity 2 is formed to receive a solid and at the
10 opposite end a bore 3 is provided which receives a rod 4 by means of which the graphite crucible 1 can be mounted in a housing 5 which is comprised of quartz glass. The housing 5 is connected in a vacuum-tight manner by a connected part 6 to a pump which has not been illustrated in FIG. 1. For special investigation, a
15 cooling finger 7 is integrated in the device and in which water driven thermally out of the sample can be collected. The housing 5, which contains the graphite crucible 1 is enclosed in a cooling jacket 8 which has a coolant inlet 9 and a coolant outlet 10. The graphite crucible 1 has bores 11a and 11b which extend
20 radially with respect to the longitudinal axis of the graphite crucible and provide a connection between the bore 3 and the environment around the graphite crucible 1. The housing 5 is surrounded at the level of the cavity 2 of the graphite crucible 1 by an induction coil 12 which is connected with a medium
25 frequency generator (MF generator). In the cooling jacket 8, at the outer sides and at the angle of 180°, two helium ducts 13 are integrated through which the carrier gas helium can flow into the housing 5 to serve as a carrier for CO or CO₂ which is to be fed

to a mass spectrometer. In the connecting part 6 there is to be found a palladium ring 14.

In the operation of the apparatus according to the invention, the graphite crucible 1, together with the solid sample, which in this example is a silicate, together with the rod 4 is introduced into the housing manually or automatically. The pump is connected via an adapter which is connected to the connection part 6. The housing 5 is comprised preferably of quartz glass since this is inert under the experimental conditions and provides no exchange of oxygen atoms at the high temperatures of the quartz glass with the oxygen produced in the experiment. The coolant jacket 8 is traversed by water supplied via the coolant inlet and which is discharged through the coolant outlet 10. The water cooling is effected in a bypass through the MF generator cooling circuit through which, via a further bypass, the induction coil is also cooled.

The induction coil is energized via the MF generator so that the graphite crucible 1 is inductively heated. The heating up time can be selected freely and can be controllable steplessly to 2200°C. The heating up, however, is required to be effected in steps. The desired temperature can be either set manually or can be programmable for an interface integrated into a network portion. According to the invention, the silicate sample, without prior purification, i.e. for example by desorption of water or OH- groups, can be decomposed in the graphite crucible 1, by the induction heating. In this manner the graphite crucible 1 is heated which results in a simultaneous heating up of the silicate sample. The temperature can be increased only slowly via the manual or programmable heating control. At a temperature of about 100 to 120°C, water can be desorbed and can

be drawn off by the pump. With further temperature increase, other impurities can be fractionatingly vaporized. Thus at a temperature of about 1000°C all OH- groups adherent to the sample are removed. Further, nitrogen groups which can quantitatively affect and falsify the latter analysis because of the molecular weight of N₂, can be driven off. At temperatures of about 1300 to 1400°C, the impurities are quantitatively removed and a further increase in the temperature results successively in a splitting off of the silicate oxygen which reacts with the graphite of the graphite crucible 1 to CO. The heating can be carried out problem-free up to a temperature of 2200°C. In these experimental conditions, there is a Boudouard equilibrium between CO and CO₂, which lies entirely to the CO side. The presence of CO, as contrasted with CO₂, has the advantage that the CO as the substance to be analyzed has up to twice as great a sensitivity with respect to mass spectrometry than CO₂. Furthermore, the experiment with CO is shorter so that processing time is saved. Thus, preferably the inductive heating is effective to the higher temperature at which the Boudouard equilibrium lies on the side of the CO. Alternatively, the CO produced by reaction of the oxygen with graphite can be transformed by a temperature lowering in the graphite crucible 1 to CO₂, based upon the Boudouard equilibrium when the equilibrium lies on the CO₂ side, the CO₂ can condense out in the cold finger 7. As a general matter in routine operations above all, the CO₂ is carried off in the helium carrier gas stream which is supplied by the helium on the feed line 13 through the connecting part or outlet 6 to the mass spectrometer. Based upon the different atomic weight of the two oxygen isotopes, the CO which is produced has a molecular weight of 28 or 30 in equilibrium with CO₂, with a molecular weight of 44

or 46. Thus it can also be advantageous to operate at a temperature which lies on the CO₂ side since its molecular weight cannot be confused with the NO₂ during the mass spectroscopic measurement in corresponding Faraday capture.

5 The method is usable for all oxygen-containing solids independently of whether they are available in powder form as amorphous masses, as crystals or some other solids form.

 The possibility of continuously heating up of the sample material replaces the prepurification of the substance
10 from undesired foreign substances or molecules by fractionated desorption or decomposition. As a result, a falsification of the output ratio of the oxygen isotopes is largely precluded since, by contrast with a chemical treatment, no exchange of oxygen atoms of the solid sample with oxygen atoms from reagents can
15 occur. With mixtures which have different decomposition temperatures or melting or vaporization temperatures, a sequential oxygen isotope determination of the different components of the mixture can be carried out.

 In an alternative embodiment of the method of the
20 invention, the sample to be analyzed or to be liberated of the investigated solid is mixed with graphite powder and this mixture is inductively heated. The mixture can optionally be pressed into a solid form.

 The graphite crucible 1 used in the apparatus according
25 to the invention can have bores 11a, 11b which provide a connection between the bore 3 for receiving the rod 4 for mounting the graphite crucible 1 in the housing 5 and the interior space of the housing 5. This is then of advantage when impurity particles have deposited in the bore 3 which can
30 interfere with the analysis. Bores 11a, 11b permit a

decomposition of these foreign particles because they facilitate discharge from the bore 3.

Basically the graphite crucible 1 can also have another geometry so that the configuration of the graphite crucible 1 is not limited to the configuration shown in FIG. 1. A circular cross section is however the best for the inductive coupling, crucible manipulation and crucible production.

The graphite should be of high purity for the analytical purposes so that no falsification of the analysis results by impurities therefrom can occur. Preferably spectral graphite is used which contains any addition of carbon or other components only in a concentration below 20 ppm with Si < 2ppm, Ca < 1ppm, B < 1ppm, Fe < 0.5ppm, Ti < 0.5ppm. Since the analysis step which follows decomposition and reaction with graphite is not limited to mass spectrometry, the purity used can deviate and have other minimum values.

The method of the invention can be used to decompose and analyze large solid quantities of for example 500 μ g in one experiment. The results are thus representative and are not subject to errors resulting from heterogeneity of the sample since in the measurement the entire sample is evaluated. Time-consuming repetitive measurements can therefore be spared.

Example:

The decomposition of silicates or opal silicon, as may occur in the shells of certain organisms like diatoms, is of special interest. The isotope ratio of oxygen contained therein can provide an indication of the ambient temperature at the time of formation of these silicon compounds. A pretreatment of these

materials has previously been necessary to remove adherent water molecules and included OH groups.

In the method used as an example, the pretreatment is carried out in a single operating step with the liberation of the oxygen and its conversion into CO or CO₂. The material to be investigated is entered into the graphite crucible and mounted in the housing 5 and functions as a high temperature cell. After evacuation of this high temperature cell to $p \approx 10^{-6}$ bar, a slow inductive heating up of the graphite crucible 1 is effected. As a result initial adsorbed water is desorbed and pumped off ($T \leq 120^{\circ}\text{C}$). With increasing temperature the included OH groups are removed. Following the ending of this procedure the material is heated up to 2000 to 2200°C at which the SiO₂ is decomposed and the oxygen reacted with the graphite of the graphite crucible 1 to CO₂ and/or CO. Based upon the Boudouard equilibrium at temperatures of about 2000°, practically only CO is present in the gas space. This can be entrained after the end of the heating step on line by means of helium as a carrier gas into the analyzer in the form of isotope mass spectrometer.

Alternatively, instead of CO, CO₂ can also be mass spectrometrically analyzed. For this purpose, after the end of the decomposition time the graphite crucible 1 is slowly cooled whereupon the Boudouard equilibrium is then shifted to the CO₂ side. After termination of the cooling step CO₂ can be entrained on line with the aid of helium as a carrier gas, analogously to the CO₂, on line, for determination of the oxygen isotope ratio measurements (flow mode).